ROOM TEMPERATURE CLEANER FLOTATION TECHNIQUE FOR SCHEELITE ROUGH CONCENTRATE①

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ABSTRACT A room temperature cleaner flotation technique was used in bench test to separate scheelite from scheelite rough concentrate containing fluorite and calcite. New depressants KSF and WTXD were used to depress fluorite and calcite stage by stage. By this technique higher-grade scheelite concentrate as well as calcite by-product were gained.

Key words scheelite flotation technique depressant

1 INTRODUCTION

In the flotation of complex scheelite ore oleic acid or sodium oleate is commonly used as collector and sodium silicate as depressant[1]. In general, by flotating the crude ore with sodium silicate and fatty acids, a scheelite-calcium mineral bulk concentrate is obtained. There are then two cleaning processes, i. e. the conventional Petrov's and acid leaching, for treating this concentrate[2-3].

Petrov's process involves steaming of bulk concentrate in 2%~4% solution of Na_2SiO_3 at 80~90 ℃, desorption of anion collector from gangue minerals, cooling, reagents removal, repulping and flotation. At acid leaching process hydrochloric acid is used to dissolve calcite or apatite. The drawback of both cleaning processes is that the operating conditions are bad and the operating costs are high.

Selective flotation of scheelite from calcium ore is rather difficult because calcite and fluorite are frequently associated with scheelite. The floatability of calcite and fluorite is very similar to that of scheelite since these minerals all contain calcium cation. A lot of effort has been taken for the separation of scheelite from other calcium minerals[4], but the results are not admirable. Phosphate modifiers were used to depress calcite and fluorite in some researches[5], and it was thought that the flowsheet of the selective flotation of scheelite with phosphate modifiers might replace the conventional Petrov's process. However, only pure mineral was investigated and the results were not verified with ores in that researches. What's more, the calcite and fluorite depressed by phosphate modifiers did not adsorb collectors before the addition of depressants, so the research was just about rough flotation of scheelite. Recent researches indicated that there is great difference in floatability between pure fluorite and fluorite which has adsorbed collector, the former can be depressed easily and the latter hardly[6]. All the scheelite, fluorite and calcite in scheelite rough concentrate have adsorbed collectors at the rough flotation, hence their separation becomes more difficult. It is the common desire of mineral processing researchers to develop a room temperature cleaner flotation technique for scheelite and get rid of the drawback of Petrov's process. The development of selective depressant is important. These de-

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pressants should quickly desorb the collector adsorbed on the surface of gangue minerals, thus the gangue minerals, such as fluorite and calcite, become water-avid and are depressed.

2 EXPERIMENTAL MATERIALS AND METHODS

2.1 Samples

The samples of pure scheelite, fluorite and calcite were ground to − 0.074 mm in a porcelain laboratory mill, and their purities were 98.8%, 98.2% and 98.7% respectively.

The scheelite ore was obtained from Shizhuyuan Mine, Hunan province. After it was crushed and ground to 90% − 0.074 mm, the magnetic minerals such as magnetite, wolframite and garnet were cleared away with magnetic separation, the sulphide minerals such as molybdenite, bismuthinite and pyrite were removed with flotation, and then scheelite rough concentrate was produced with flotation of high alkalinity pulp (pH > 12). The composition of rough concentrate was 6.32% WO_3, 72.00% $CaCO_3$ and 13.5% CaF_2.

2.2 Flotation tests and reagents

The flotation tests of pure minerals and scheelite ore were carried out in a XFG and a model XFD laboratory flotation cell, respectively. The depressants were KSF and WTXD. KSF is such a compound that it can produce SiO_3^{2-}, F^-, $HSiO_3^-$ and other anions in its aqueous solution. WTXD is an aqueous solution consisting of sodium silicate and TXD (by a mass ratio of 1 to 1), and the latter is an acid containing P element.

2.3 Measurements of adsorption of reagents on mineral surface

The adsorption of sodium oleate on mineral surface was measured with UV− 3000 model ultraviolet spectrometer made in Japan, the adsorption of KSF was measured through chemical analysis, and the qualitative analysis of the adsorption and reaction of TXD on mineral surface was carried out with photoelectron energy spectrometer.

3 RESULTS AND DISCUSSION

In following tests the mineral froth product is defined as the concentrate of pure mineral flotation with such condition: NaOH 100 mg·L^{-1}, sodium oleate 100 mg·L^{-1}, pine camphor oil 50 mg·L^{-1}, flotation time 2 min and pulp temperature 18~ 20 ℃. This froth product have already adsorbed sodium oleate, its floatability is different from that of pure mineral.

3.1 Depression of fluorite and adsorption of reagents

In flotation tests of froth product of scheelite, calcite and fluorite with KSF as depressant, it was found that KSF can depress fluorite strongly, scheelite and calcite weakly, as shown in Fig. 1.

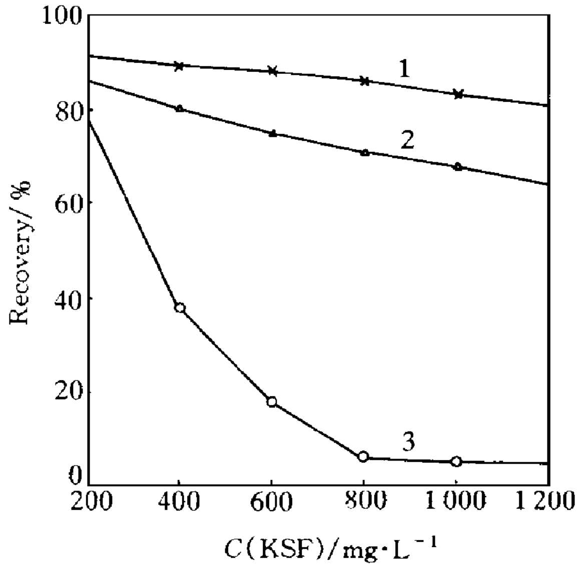

Fig. 1 Effect of KSF on floatability of froth product

1 —scheelite; 2 —calcite; 3 —fluorite

The mechanism that KSF selectively depress fluorite is that it can conduct a competitive adsorption with sodium oleate on the liquid-solid interface. When KSF is added into the pulp, it is absorbed on fluorite surface and at the same time the sodium oleate absorbed on the surface is desorbed.

The adsorption of KSF and the surplus adsorption of sodium oleate on fluorite surface at different KSF concentration were measured. The relation between adsorption of KSF and surplus adsorption of sodium oleate at the same KSF concentration with the former as horizontal and the latter as vertical lines is shown in Fig 2. It shows that there is almost a straight line between the relation of adsorption capacity of KSF and surplus adsorption capacity of sodium oleate. From the stretch of the line it is found that the slope rate $a = -2.67/35 = -0.076$, and the cutting distance $b = 2.67$, so the line can be expressed as such a formula:

$$Y = -0.076X + 2.67$$

where Y is surplus adsorbing capacity of sodium oleate, X is adsorbing capacity of KSF.

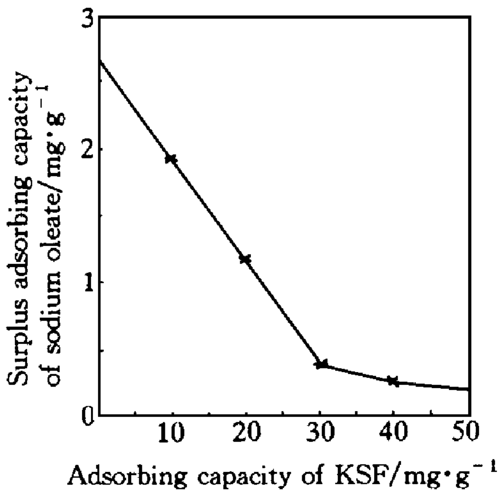

Fig. 2 Influence of adsorption of KSF on surplus adsorption of sodium oleate

According to this formula the surplus adsorbing capacity of sodium oleate corresponding to a certain adsorbing capacity of KSF can be calculated. For example, when adsorbing capacity of KSF is 35 mg·L^{-1}, the surplus adsorbing capacity of sodium oleate is:

$$Y = -0.076 \times 35 + 2.67 = 0$$

that means the sodium oleate is desorbed completely.

The flotation tests and measurements showed KSF is an effective depression for fluorite froth product. This conclusion can be further confirmed by the separation tests of froth product mixture, as given in Table 1.

With a flowsheet of 1 rougher and 2 cleaners to separate the froth product mixture, and the KSF concentration was 400 mg·L^{-1} for rougher, 100 mg·L^{-1} for each cleaner, a concentrate with scheelite grade 76.54% WO_3, scheelite recovery 84.30% was gained.

Table 1 Result of scheelite concentration after one rougher from mixture of froth product

C(KSF)/mg·L^{-1}	WO_3 grade/%	WO_3 recovery/%
300	50.81	94.66
400	52.49	94.31
500	53.85	93.17
600	55.17	90.24

Remarks: The mixture of froth product was made of 6.0 g fluorite and 0.5 g scheelite, the feed grade was 6.2%, and KSF was agitated for 5 min.

3.2 Depression of calcite and mechanism

After depression of fluorite with KSF as depressant in the separation of scheelite rough concentrate containing both fluorite and calcite, acid leaching may be used to remove calcite so as to produce scheelite concentrate. Nevertheless, it is more important for mineral processing researchers to develop new depressants with which calcite can be depressed and separation of scheelite from calcite can be realized.

A previous study showed that one compound TXD containing P element is a selective depressant for calcite[7], so we got a mixture WTXD, which was mixed with TXD and sodium silicate in a mass ratio of 1 to 1. The effect of WTXD on froth product of scheelite and calcite is shown in Fig 3, it indicates that under the circumstances of suitable concentration WTXD depressed calcite strongly and scheelite weakly.

The depression mechanism of WTXD can be explained in two aspects. One is that TXD is a kind of phosphoric acid which can form hydrophilic calcium salt of TXD on calcite surface, another is that TXD can make sodium silicate acidic and improve its selective depression ability. The calcium salt of TXD is hydrophilic, sodium oleate cannot be absorbed on its surface.

The X-ray photoelectron spectra measurements of pure calcite and the calcite acted by TXD were made previously in another paper[7]. The results showed that the calcite acted by

TXD has P_{2p} and P_{2s} waves at the points of about 140 and 195eV binding energy. but the pure calcite has no such waves . This indicates that after calcite has been acted by TXD, its surface contains TXD, because the element P is provided by TXD. Therefore X- ray photoelectron spectra measurements confirm that adsorption and chemical reaction of TXD on calcite surface result in depression of calcite.

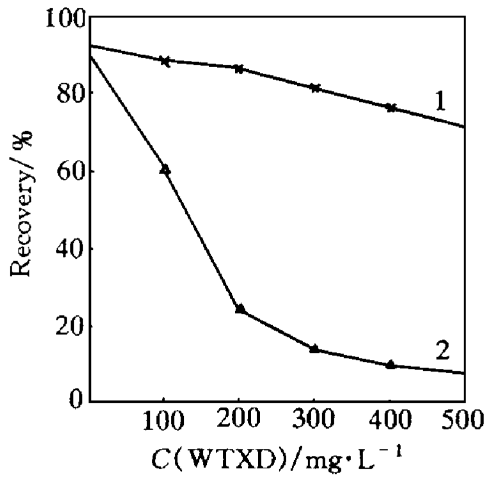

Fig. 3 Effect of WTXD on floatability of froth product

1 —scheelite; 2 —calcite

Table 2 is the result of a separation test of mineral mixture through 1 rougher and 1 cleaner. The mineral mixture was made of 1g scheelite froth product and 9g calcite froth product.

Table 2 Result of scheelite concentrate after one rougher and one cleaner from mixture of froth product

C(WTXD) / mg·L^{-1}		Scheelite concentrate	
rougher	cleaner	WO_3 grade/ %	WO_3 recovery/ %
400	100	70. 50	92. 00
400	200	73. 40	91. 30
600	100	75. 65	90. 38
600	200	76. 85	90. 00

The result showed that separation of scheelite from calcite can be realized with WTXD as depression, when the grade of mineral mixture was 8. 06% WO_3, a scheelite concentrate of grade 76. 85% WO_3 and recovery 90. 00% were gained through 1 rougher and 1 cleaner.

3. 3 Separation test of scheelite ore

A new technique, which is named "stage by stage depression technique" in this paper, was used to separate scheelite from fluorite and calcite. That is, at room temperature around 22 ℃, depressing fluorite with KSF at the first stage, and dispersing or depressing other slimes with 100g/ t sodium silicate; then at the second stage depressing calcite with WTXD. Fig. 4 is the basic technological flowsheet.

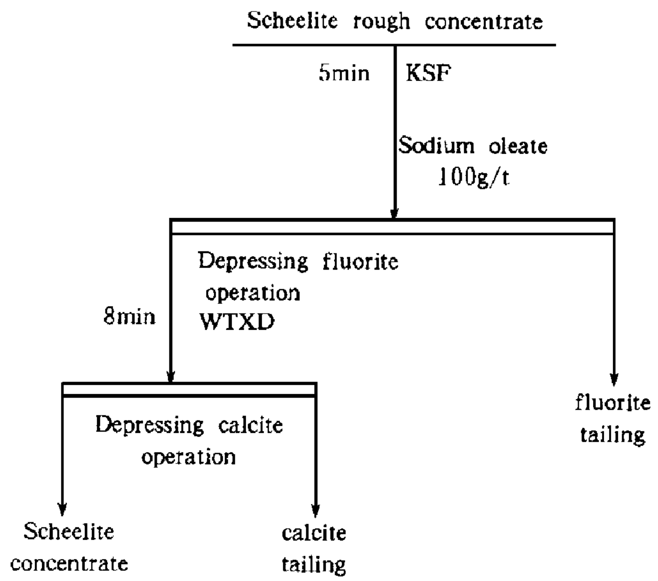

Fig. 4 Basic flowsheet of room temperature cleaner

The operation of depressing fluorite involved 1 rougher, 1 scavenger and 1 cleaner. The KSF concentration was 600, 100, and 400g/ t for rougher, scavenger and cleaner respectively. The result of an open-circuit test is shown in Table 3.

Following the first stage was the second operation where calcite was depressed with WTXD. This stage involved 1 rougher, 1 scavenger and 2 cleaners, in which the dosage of WTXD was 800, 100, 400 and 200 g/ t respectively. Table 4 presents the result.

Then, on the basis of the open-circuit test, a locked cyclic batch test was carried out, where the middlings were sent back step by step and

Table 3 Open-circuit test result of depressing fluorite

Product	Yield /%	Grade/%			Recovery/%
		WO_3	CaF_2	$CaCO_3$	WO_3
Mixture concentrate of scheelite and calcite	65.50	8.13	1.36	87.50	84.25
Middling	19.00	4.93	9.74	59.88	14.82
Fluorite tailing	15.50	0.37	69.42	21.35	0.93
Scheelite rough concentrate	100.00	6.32	13.50	72.00	100.00

Table 4 Open-circuit test result of depressing fluorite

Product	Yield /%	Grade/%		Recovery/%
		WO_2	$CaCO_3$	WO_3
Concentrate	9.48	72.30	7.55	84.28
Middling 2	3.45	20.41	69.34	8.66
Middling 1	2.92	10.14	76.30	3.64
Calcite tailing	84.15	0.33	97.64	3.42
Feed	100.00	8.13	87.50	100.00

other conditions unchanged. A concentrate with grade 71.00% WO_3 and scheelite recovery 91.67% were gained, as well as a calcite by-product with grade 97.15% $CaCO_3$.

4 CONCLUSION

KSF and WTXD are effective depressants of fluorite and calcite, respectively. In the cleaner flotation tests the separation of scheelite from scheelite rough concentrate containing fluorite and calcite was realized at room temperature by a "stage by stage depression technique". At the first stage, fluorite was selectively depressed by KSF, which can desorbed the sodium oleate and itself be absorbed on fluorite surface. Then at the second stage, calcite was depressed by WTXD, which was mixed with sodium silicate and TXD. Besides making sodium silicate acidic and improving its selective depression ability, TXD can be adsorbed and produce hydrophilic calcium salt on calcite surface. The effective depression of WXTD on calcite is due to the chemical adsorption and reaction.

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